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EP-A- 0 218 215 EP-A- 0 228 525
EP-A- 0 296 473 EP-A- 0 315 865
EP-A- 0 359 366 WO-A-85/02622
US-A- 4 624 972

Römpps Chemie-Lexikon, Achte Auflage,
Franckh'sch Verlagshandlung, Stuttgart,
1981, page 1721

Plastic Terminology Dictionary, page 425,
Sept. 10, 1989.

(73) Proprietor: MITSUBISHI GAS CHEMICAL COMPANY, INC.
5-2, Marunouchi 2-chome
Chiyoda-Ku
Tokyo, 100 (JP)

(72) Inventor: Mizutani, Makoto Mitsubishi Gas
Chemical Co. Inc.
6-2, Higashiyahata 5-chome
Hiratsuka-shi
Kanagawa (JP)
Inventor: Nagai, Satoshi Mitsubishi Gas
Chemical Co. Inc.
6-2, Higashiyahata 5-chome
Hiratsuka-shi
Kanagawa (JP)
Inventor: Masumoto, Mitsuhiko Mitsubishi
Gas Chemical Co. Inc.
12, Kamisu-cho 2-chome
Tyonaka-shi
Osaka (JP)
Inventor: Aso, Toshiaki Mitsubishi Gas
Chemical Co. Inc.
12, Kamisu-cho 2-chome
Tyonaka-shi
Osaka (JP)

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⑦4 Representative: Brauns, Hans-Adolf, Dr. rer.
nat. et al
Hoffmann, Eitle & Partner
Patentanwälte
Postfach 81 04 20
D-81904 München (DE)

Description**FIELD OF THE INVENTION**

5 The present invention relates to a polycarbonate resin composition having excellent radiation resistance. Moulded articles produced by using the polycarbonate resin composition of this invention undergo only little yellowing when exposed to radiation in the air or under an atmosphere of substantially no oxygen, and can be advantageously employed in medical appliances to be used after radiation-sterilization in the air or under an oxygen-free atmosphere.

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BACKGROUND OF THE INVENTION

Aromatic polycarbonate resins are frequently used in medical products due to their high impact resistance, heat resistance, and transparency and good safety.

15 For application of aromatic polycarbonates in medical products, the high-pressure steam sterilization method and the ethylene oxide gas (EOG) sterilization method have conventionally been employed. However, the steam sterilization method has disadvantages that complete sterilization is difficult and the treatment procedures have drawbacks such as the necessity of a drying step after the sterilization. Further, the EOG sterilization method has problems such as the toxicity of residual EOG absorbed in the sterilized

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materials.

For this reason, attention is recently focused on radiation sterilization in which products to be sterilized are exposed to radiation (generally, gamma rays and electron beams) and which can be practiced at relatively low costs under a low temperature and dry atmosphere, and also focused on oxygen-free radiation sterilization in which products are sterilized under substantially oxygen-free conditions for the purposes of

25 suppressing the multiplication of microorganisms and preventing the deterioration of hollow fibers made of cellulose acetate, etc.

However, polycarbonate resin moulded articles conventionally used in those fields have a defect that upon exposure to radiation, the articles suffer yellowing due to the decomposition of the resin, thus lessening the value of the products. This tendency becomes very strong where the radiation sterilization is

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35 conducted under substantially oxygen-free atmosphere.

JP-A-62-135556 discloses a composition which is prepared by blending a polyether polyol or its alkyl ether with an ordinary polycarbonate resin containing no halogen, thereby showing improved resistance to yellowing caused by irradiation. (The term "JP-A" as used herein means an "unexamined published Japanese patent application".) However, the improvement in diminishing the irradiation-caused yellowing is insufficient, and particularly, in a substantially oxygen-free atmosphere, almost no effects are brought about. In addition, the above-proposed polycarbonate resin composition is defective in that the addition of a polyether polyol or its alkyl ether often results in poor heat stability of the composition.

SUMMARY OF THE INVENTION

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The present inventors have conducted intensive studies to develop a polycarbonate resin composition which can be molded into medical products suitable for sterilization by irradiation. As a result, they have found that a polycarbonate resin composition obtained by blending a poly(alkylene glycol) or its ether, silyl ether, or ester with an aromatic polycarbonate containing in its molecular chain a structural unit derived from a halogenated bisphenol can be greatly prevented from suffering yellow discoloration even where radiation sterilization is performed under substantially oxygen-free atmosphere, as well as in the air. This invention has been completed based on the above finding.

The polycarbonate resin composition for radiation sterilization according to the present invention comprises

50 (A) an aromatic polycarbonate resin containing an aromatic polycarbonate polymer or oligomer having in its molecular chain a structural unit derived from a halogenated bisphenol and,

(B) a polyalkylene compound selected from the group consisting of poly(alkylene glycol)s, poly(alkylene glycol) ethers, poly(alkylene glycol) silyl ethers and poly(alkylene glycol) esters and represented by the following formula (1):

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wherein R represents hydrogen or a lower alkyl group (e.g., methyl or ethyl), X¹ and X² each represents

hydrogen, an alkyl group having 1 to 10 carbon atoms, an acyl group having 2 to 35 carbon atoms, an aryl group having 6 to 12 carbon atoms, or -Si(R¹)₃ group, wherein R¹ which may be the same or different each represents an alkyl group having 1 to 10 carbon atoms or an aryl group having 6 to 10 carbon atoms, and m is an integer up to 1,000.

5 In preferred embodiments of this invention, the aromatic polycarbonate resin (A) has a halogen content in the range of from 0.1 to 10% by weight, more preferably from 0.5 to 5% by weight; the amount of the polyalkylene compound (B) of the formula (1) added is in the range of from 0.1 to 5% by weight, more preferably from 0.1 to 3% by weight, and the (B) is an ester.

In other preferred embodiments, the polycarbonate resin composition of this invention further comprises
10 at least one release agent selected from the group consisting of esters of saturated higher fatty acids with saturated alcohols, paraffins, and low molecular weight polyolefins, the amount of the at least one release agent added to the composition being in the range of from 0.01 to 3% by weight, more preferably from 0.1 to 1% by weight, and/or at least one heat stabilizer selected from the group consisting of phosphorous acid and phosphorous esters, the amount of the at least one heat stabilizer added to the composition being in
15 the range of from 0.001 to 0.1% by weight.

DETAILED DESCRIPTION OF THE INVENTION

The aromatic polycarbonate polymer or oligomer, which constitutes component (A) of the composition
20 of this invention and contains in its molecular chain a structural unit derived from a halogenated bisphenol, is an aromatic polycarbonate resin or oligomer which is produced using a halogenated bisphenol as part or all of the dihydric phenol(s) and which itself is conventionally known. Preferred examples thereof include (a) an aromatic polycarbonate copolymer produced using a halogenated bisphenol as part of the dihydric phenols, (b) an aromatic polycarbonate homooligomer produced using a halogenated bisphenol as the
25 dihydric phenol, and (c) an aromatic polycarbonate cooligomer produced using a halogenated bisphenol as part of the dihydric phenols. Although halogenated bisphenol monomers are also effective in the prevention of yellowing by irradiation, they are not so preferred because of their poor heat stability.

Specific examples of the aromatic polycarbonate resin (A) in the composition of this invention include:
30 (1) an aromatic polycarbonate resin consisting of the above (a) alone; (2) a composition consisting of (a) above and any of the above (b) and (c) and an aromatic polycarbonate oligomer derived from a dihydric phenol containing no halogen; and (3) a composition consisting of an aromatic polycarbonate resin derived from a dihydric phenol containing no halogen and any of the above (a), (b), and (c).

Examples of the halogenated bisphenol include bis(4-hydroxy-3,5-dibromophenyl)methane, 2,2-bis(4-hydroxy-3,5-dibromophenyl)propane, 4,4'-dihydroxy-3,3',5,5'-tetrabromodiphenylsulfide, 2,2-bis(4-hydroxy-3,5-dichlorophenyl)propane, 2,2-bis(4-hydroxy-3-bromophenyl)propane, bis(4-hydroxy-3-chlorophenyl)-methane, bis(4-hydroxy-3,5-dichlorophenyl)methane, and bis(4-hydroxy-3-bromophenyl)methane. Examples of the dihydric phenol containing no halogen include bis(4-hydroxyphenyl)methane, bis(4-hydroxyphenyl)ether, bis(4-hydroxyphenyl) sulfone, bis(4-hydroxyphenyl) sulfoxide, bis(4-hydroxyphenyl) sulfide, bis(4-hydroxyphenyl) ketone, 1,1-bis(4-hydroxyphenyl)ethane, 2,2-bis(4-hydroxyphenyl)propane, 2,2-bis(4-hydroxyphenyl)butane, 1,1-bis(4-hydroxyphenyl)cyclohexane, 2,2-bis(4-hydroxy-3,5-dimethylphenyl)propane, 1,1-bis(4-hydroxyphenyl)-1-phenylethane, and bis(4-hydroxyphenyl)diphenylmethane.

Examples of terminators (molecular weight modifiers) which can be used in the production of the aromatic polycarbonate polymer or oligomer include ordinarily employed ones such as phenol, p-t-butylphenol, and tribromophenol. In addition to these, examples thereof further include: long chain alkyl-substituted phenols such as octylphenol, nonylphenol, laurylphenol, palmitylphenol, and stearylphenol; long chain alkyl esters of hydroxybenzoic acid such as octyl hydroxybenzoate, lauryl hydroxybenzoate, nonyl hydroxybenzoate, and stearyl hydroxybenzoate; (long chain alkyl)oxyphenols such as octyl ether phenol (=octyloxyphenol), nonyl ether phenol, lauryl ether phenol, palmityl ether phenol, octadecyloxyphenol, and dodecyloxyphenol; and aliphatic acid chlorides such as capric acid chloride, lauric acid chloride, myristic acid chloride, palmitic acid chloride, stearic acid chloride, and cerotic acid chloride.

In producing the aromatic polycarbonate polymer or oligomer according to this invention, a chain-branching agent may be used in combination with the chain terminator in an amount of from 0.01 to 3 mol, preferably from 0.1 to 1.0 mol, per 100 mol of the dihydric phenol compound, thereby to give a branched polycarbonate. Examples of such chain-branching agent include polyhydroxy compounds such as phloroglucinol, 2,6-dimethyl-2,4,6-tri(4-hydroxyphenyl)heptene-3, 4,6-dimethyl-2,4,6-tri(4-hydroxyphenyl)-heptene-2, 1,3,5-tri(2-hydroxyphenyl)benzole, 1,1,1-tri(4-hydroxyphenyl)ethane, 2,6-bis(2-hydroxy-5-methylbenzyl)-4-methylphenol, and α,α',α'' -tri(4-hydroxyphenyl)-1,3,5-triisopropylbenzene, and further include 3,3-bis(4-hydroxyaryl)oxyindol (=isatin bisphenol), 5-chloroisatin, 5,7-dichloroisatin, and 5-bromoisatin.

Of the above-described polycarbonates, examples of polycarbonate resin (A) which are preferably used in producing the polycarbonate resin composition for radiation sterilization according to this invention include: (1) a copolycarbonate resin derived from 2,2- bis(4-hydroxyphenyl)propane (=bisphenol A) and 2,2-bis(4-hydroxy-3,5-dibromophenyl)propane (=tetrabromobisphenol A); (2) a composition comprised of bisphenol A polycarbonate resin and the copolycarbonate resin (1) above; and (3) a composition comprised of bisphenol A polycarbonate resin and either of a tetrabromobisphenol A polycarbonate oligomer terminal-blocked with p-t-butylphenol, tribromophenol, etc. and a terminal-blocked copolycarbonate oligomer derived from bisphenol A and tetrabromobisphenol A.

A too low or too high halogen atom content in the composition of this invention (or in the polycarbonate resin) is not preferred, because the effect of preventing irradiation-caused yellow discoloration cannot be produced with too low halogen atom content, while too high halogen atom content impairs the mechanical properties and heat resistance of the composition. Therefore, the halogen atom content in the polycarbonate resin (A) is preferably from 0.1 to 10% by weight, more preferably from 0.3 to 5% by weight.

The polyalkylene compound of component (B) according to the present invention is obtained by the ring-opening polymerization of an alkylene oxide such as ethylene oxide, propylene oxide, or butylene oxide. In this invention, such polyalkylene compound can be used as it is, or after being etherified, silyl-etherified, or esterified.

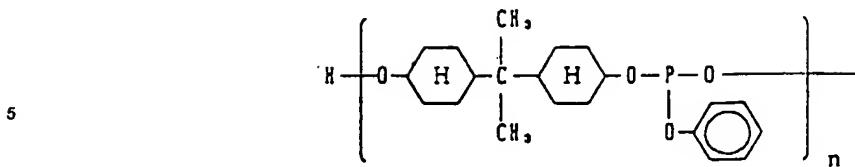
Specific examples of component (B) include poly(alkylene glycol)s such as poly(ethylene glycol) and poly(propylene glycol); alkyl-etherified products such as poly(ethylene glycol) dimethyl ether, poly(propylene glycol) dimethyl ether, poly(ethylene glycol) diethyl ether, poly(propylene glycol) diethyl ether, poly(ethylene glycol) dipropyl ether, poly(propylene glycol) dipropyl ether, poly(ethylene glycol) dibutyl ether, and poly(propylene glycol) dibutyl ether; silyl-etherified products such as reaction products of poly(propylene glycol) with chlorotrimethylsilane or chlorotriethylsilane; and esters of poly(alkylene glycol)s with aliphatic or aromatic carboxylic acids, such as poly(ethylene glycol) diacetate, poly(propylene glycol) diacetate, poly(ethylene glycol) dipropionate, poly(propylene glycol) dipropionate, poly(ethylene glycol) distearate, poly(propylene glycol) distearate, poly(propylene glycol) dilaurate, and poly(propylene glycol) dibehenate. Of these, poly(alkylene glycol) esters are most preferably used.

The amount of component (B) in the composition is from 0.1 to 5% by weight, preferably from 0.3 to 3% by weight, based on the weight of compound (A). If the amount thereof is below 0.1% by weight, the yellowing by irradiation cannot be prevented sufficiently. On the other hand, an amount thereof exceeding 5% by weight is not preferred in that not only the effect of preventing yellow discoloration cannot be heightened any more, but also the mechanical properties and heat resistance of the composition are impaired.

The composition of this invention, which comprises the above-described components (A) and (B) as essential components, may preferably further contain a release agent in order to improve moldability of the composition. It is also preferred to add a heat stabilizer for improving heat stability of the composition.

The release agent is not particularly limited so long as it is a known release agent which is generally used for polycarbonate resins and contains substantially no olefinically unsaturated carbon-carbon double bonds in its molecule. Examples of such release agent include: esters or partial esters of saturated higher fatty acids (such as stearic acid, palmitic acid, myristic acid, and behenic acid) with saturated alcohols (such as butyl alcohol, hexyl alcohol, octyl alcohol, nonyl alcohol, lauryl alcohol, myristyl alcohol, stearyl alcohol, behenyl alcohol, ethylene glycol, propylene glycol, butanediol, hexanediol, glycerin, butanetriol, pentanetriol, erythritol, and pentaerythritol); and waxes such as paraffins, low molecular weight polyolefins, and others. Particularly preferred of these are, for example, glyceryl monostearate, glyceryl distearate, glyceryl tristearate, pentaerythritol tetraestearate, pentaerythritol tetrabehenate, pentaerythritol tetralaurate, and pentaerythritol tetramyrystate. The amount of the release agent added is from 0.01 to 3% by weight, preferably from 0.1 to 1% by weight, based on the weight of component (A).

The heat stabilizer is preferably selected from phosphorous acid and phosphorous esters. Examples thereof include phosphorous acid, triphenyl phosphite, tris(nonylphenyl) phosphite, tris(2-ethylhexyl) phosphite, tridecyl phosphite, tristridecyl phosphite, diphenyl mono(2-ethylhexyl) phosphite, diphenyl monodecyl phosphite, diphenyl monotridecyl phosphite, dilauryl hydrogen phosphite, diphenyl hydrogen phosphite, tetraphenyl di(propylene glycol) diphosphite, tetratridecyl 4,4'-isopropylidenediphenyl phosphite, triauryl trithiophosphite, bistridecyl pentaerythritol diphosphite, bisnonylphenyl pentaerythritol diphosphite, bis(2,4-di-t-butylphenyl) pentaerythritol diphosphite, bis(2,6-di-t-butylphenyl) pentaerythritol diphosphite, distearyl pentaerythritol diphosphite, and tris(2,4-di-t-butylphenyl) phosphite, and also include hydrogenated bisphenol A phosphite polymer typically represented by the following formula.



10 Preferred of these heat stabilizers are phosphorous acid, tris(2,4-di-t-butylphenyl) phosphite(M2112),tris(nonylphenyl) phosphite, bis(2,4-di-t-butylphenyl) pentaerythritol diphosphite (PEP24), bis(2,6-di-t-butylphenyl) pentaerythritol diphosphite (PEP36), distearyl pentaerythritol diphosphite (PEP8), and hydrogenated bisphenol A phosphite polymer (HBP). The amount of the heat stabilizer added to the composition is from 0.001 to 0.1% by weight based on the weight of component (A).

15 Using the above-described components, the polycarbonate resin composition of this invention can be usually obtained by mixing the components simultaneously or successively, extruding the resulting mixture by means of an extruder having a cylinder temperature of 250 to 320 °C, and then shaping the extrudate into pellets. Conditions under which the thus-obtained composition of the invention is formed into polycarbonate molded articles for radiation sterilization vary depending upon the viscosity average molecular weight of the aromatic polycarbonate resin used, kind of the dihydric phenol used, kind of the terminator, kind and amount of the polyalkylene compound, kind and amount of the release agent, content of the halogenated bisphenol, etc. In general, however, molded articles are manufactured by injection molding at 260 to 340 °C.

20 Although the polycarbonate resin composition of this invention, from which polycarbonate molded articles for radiation sterilization can be produced, comprises the above-described essential components (A) and (B) and if required and necessary, further comprises a release agent and a heat stabilizer as described above. Further, other additives not denaturing under irradiation may be added thereto according to need for the purpose of improving moldability and for other purposes.

25 The present invention will be now explained in more detail by reference to the following Synthesis Examples, Examples, and Comparative Examples, in which all percents and parts are by weight unless otherwise indicated.

Synthesis Example 1

30 Into a 100 liter reactor were introduced 8.1 kg of bisphenol A (hereinafter referred to as "BPA"), 750 g of tetrabromobisphenol A (hereinafter referred to as "TBA"), 42 liters of 9% aqueous sodium hydroxide solution, and 30 liters of methylene chloride (hereinafter referred to as "MC"). 4.2 kg of phosgene was blown into the resulting mixture over a period of 30 minutes, while the mixture was being stirred and maintained at about 20 °C.

35 40 209 g of p-tert-butylphenol (hereinafter referred to as "PTBP") dissolved in 2 liters of MC and 7 ml of triethylamine (hereinafter referred to as "TEA") were added to the above-obtained reaction mixture, and stirring was continued for about 1 hour to proceed polymerization.

45 The resulting polymerization mixture was separated into an aqueous phase and an organic phase. The organic phase was neutralized with phosphoric acid, and then washed with water repeatedly until the pH of the washings became neutral. 35 liters of isopropanol was added to the organic phase to precipitate the polymer formed. The precipitate was filtered off and then dried, thereby obtaining a white powdery polycarbonate copolymer (hereinafter referred to as "C-PC").

The viscosity average molecular weight of the C-PC was 25,000, and the bromine (Br) content was 4.46% as calculated from the amount of the monomer reacted in the polymerization.

Synthesis Example 2

50 Into a 100 liter reactor were introduced 9 kg of TBA, 30 liters of 9% aqueous sodium hydroxide solution, 10 liters of water, 23 liters of MC, and 6 ml of TEA. 2.5 kg of phosgene was blown into the resulting mixture over a period of 30 minutes, while the mixture was being stirred and maintained at about 20 °C.

55 970 g of PTBP dissolved in 10 liters of MC and 50 ml of TEA were added to the above-obtained reaction mixture, and stirring was continued for about 1 hour to proceed polymerization.

The resulting organic phase was purified in the same manner as in Synthesis Example 1 above, and the solvent in the organic phase was then evaporation-removed to obtain a dry residue. Thus, there was obtained a white powdery polycarbonate homooligomer (hereinafter referred to as "HO-PC") having an average degree of polymerization of 5 and a Br content of 50.3%.

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Synthesis Example 3

10 Into a 100 liter reactor were introduced 9.8 kg of TBA, 30 liters of water, 37 liters of MC, 4 liters of 9% aqueous sodium hydroxide solution, and 4.9 g of triethylbenzylammonium chloride. 3.8 kg of phosgene was blown into the resulting mixture over a period of 30 minutes, while the pH and temperature of the mixture were maintained at 11.0 to 11.8 and about 20°C, respectively. The pH adjustment was conducted by adding 35% aqueous sodium hydroxide solution.

15 The reaction mixture was subsequently transferred to a 150 liter reactor, and a solution prepared by dissolving 19 liters of 9% aqueous sodium hydroxide solution, 2.2 kg of BPA, and 1.65 kg of PTBP in 15 liters of MC was added to the transferred reaction mixture. Further, 450 g of TEA was added thereto, and stirring was continued for about 1 hour to proceed polymerization.

20 The resulting reaction mixture was treated in the same manner as in Synthesis Example 2 above, thereby obtaining a white powdery polycarbonate cooligomer (hereinafter referred to as "CO-PC") having an average degree of polymerization of 5 and a Br content of 39.7%.

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EXAMPLES 1 to 13 AND COMPARATIVE EXAMPLES 1 to 7

25 Various polycarbonate resin compositions were prepared by appropriately blending the following ingredients in various proportions as shown in Tables 1 to 3 by means of a tumbler: an aromatic polycarbonate resin (trade name "Iupilon S-3000", manufactured by Mitsubishi Gas Chemical Company, Inc., Japan), the polycarbonate polymers or oligomers as obtained in Synthesis Examples 1 to 3; the poly-(alkylene glycol)s or poly(alkylene glycol) esters as specified below; pentaerythritol tetraesterate (hereinafter referred to as "PTS", containing no unsaturated double bond) or beeswax (hereinafter referred to as "BW", containing an unsaturated double bond), as a release agent; and tris(2,4-di-t-butylphenyl) phosphite (hereinafter referred to as "M2112"), bis(2,4-di-t-butylphenyl) pentaerythritol diphosphite (hereinafter referred to as "PEP24"), or bis(2,6-di-t-butylphenyl) pentaerythritol diphosphite (hereinafter referred to as "PEP36"), as a heat stabilizer. Each of the resulting mixtures was extruded with a single-screw vented extruder and formed into pellets.

35 The thus-obtained pellets were molded into 3.2mm thick test pieces having a size of 50mm x 60mm by means of an injection molding machine (Neomat 110/45, manufactured by Sumitomo Heavy Industries, Ltd., Japan) at a resin temperature of 300°C, a mold temperature of 80°C, and an injection pressure of 1,200 kg/cm².

40 These molded test pieces were divided into two groups, and those in one group were irradiated in the air with 2.5 megarad gamma rays and those in another group were sealed together with a deoxidant (trade name "Ageless", manufactured by Mitsubishi Gas Chemical Company) and irradiated under oxygen-free conditions with 2.5 megarad gamma rays. The changes ($\Delta Y.I.$) in yellowness index (Y.I.) were measured with color difference meter SM-3-CH, manufactured by Suga Shikenki Co., Ltd., Japan.

45 Further, for the evaluation of heat stability, the viscosity average molecular weight (M_v) was measured before and after pellets were allowed to stand in a nitrogen atmosphere at 340°C for 1 hour, and the difference therebetween was measured.

The results obtained are shown in Tables 1 to 3, in which the following abbreviations are used.

S-3000:	Aromatic polycarbonate resin containing no halogen.
C-PC:	Aromatic polycarbonate resin containing 4.46% Br.
HO-PC:	Aromatic polycarbonate homooligomer containing 50.3% Br.
50 CO-PC:	Aromatic polycarbonate cooligomer containing 39.7% Br.
PEG10:	Poly(ethylene glycol) having a molecular weight of 1,000.
PPG20:	Poly(propylene glycol) having a molecular weight of 2,000.
PEGST30:	Poly(propylene glycol) distearate having a molecular weight of 3,000.
PPGPR40:	Poly(propylene glycol) dibutyrate having a molecular weight of 4,000.
55 PPGOC20:	Poly(ethylene glycol) dicaprylate having a molecular weight of 2,000.
PTS:	Pentaerythritol tetraesterate.
BW:	Beeswax.
M2112:	Tris(2,4-di-t-butylphenyl) phosphite.

PEP24: Tris(2,4-di-t-butylphenyl) pentaerythritol diphosphite.
 PEP36: Tris(2,6-di-t-butyl-4-methylphenyl) pentaerythritol diphosphite.
 Mv: Viscosity average molecular weight as measured at 25°C in 0.5 g/dl MC solution.

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Table 1

		Example					
		1*	2*	3*	4*	5*	6*
10		S-3000	50	50	95	95	80
	Polycarbonate resin	C-PC	50	50		20	4
		HO-PC			5		1
15	Components	CO-PC			5		
	(parts)	PEG10	1.0				
	Poly(alkylene glycol) or its ester	PPG20		1.0	1.0	1.0	
		PPGST30				0.7	
		PPGPR40					0.6
20		PEGOC20					
	Br content (%)	(%)	2.23	2.23	2.52	2.0	0.89
						0.68	
	Before γ -ray irradiation		3.1	3.0	2.9	3.0	3.0
25	Y.I.	After γ -ray irradiation	In air	9.1	8.7	8.5	9.9
		Oxygen-free		6.8	6.7	7.0	7.8
						6.7	8.1
						7.0	
30	Δ Y.I.	In air		6.0	5.7	5.6	7.1
		Oxygen-free		3.7	3.7	4.1	4.8
						4.7	5.2
						3.7	4.1

* not example of this invention

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Table 2

			Example						
			7	8	9*	10	11	12	13
5		S-3000	50	70	97	97	70	70	70
10	Components	Polycarbonate resin	C-PC HO-PC CO-PC	50 30 3			30	30	30
15	(parts)	Poly(alkylene glycol) or its ester	PPG10 PPG20 PPGST30 PPGPR40 PEGOC20	1.0 0.5 1.0 0.7			0.5	0.5	0.5
20		Release agent	PTS	0.3	0.1		0.05	0.1	0.1
25		Heat stabilizer	M2112 PEP24 PEP36				0.05	0.05	0.05
30	Br content	(%)	2.23	1.34	1.51	1.20	1.34	1.34	1.34
35	Before γ -ray irradiation		2.9	2.7	2.6	2.8	2.6	2.5	2.5
40	Y.I.	After γ -ray irradiation	In air Oxygen-free	9.5 7.0	7.2 6.0	7.0 5.7	7.5 6.5	8.0 5.8	7.0 5.6
45	Δ Y.I.		In air Oxygen-free	6.6 4.1	4.5 3.3	4.4 3.1	4.7 3.7	4.4 3.2	4.5 3.1
50	Heat Stability Viscosity-average molecular weight ($M_v \times 10^{-3}$)	Before treatment After treatment Decrease	-	22	22	22	22	22	22

* not example of this invention

Table 3

		Comparative Example						
		1	2	3	4	5	6	7
5	Polycarbonate resin	S-3000 C-PC	100 100	100	70 30	50 50	70 30	50 50
10 Components (parts)	Poly(alkylene glycol)	PEG10 PPG20	1.0				1.0	1.0
	Release agent	BW					0.3	0.3
	Br content (%)		0	0	0	1.34	2.23	1.34
Before γ -ray irradiation		3.0	2.8	2.8	2.8	2.8	2.7	3.0
20 Y.I.	After γ -ray irradiation	In air	32.7	32.0	32.0	13.4	11.3	31.6
		Oxygen-free	57.6	48.2	48.2	8.5	7.7	61.2
	Δ Y.I.	In air	29.7	29.2	29.2	10.6	8.5	28.9
		Oxygen-free	54.6	45.4	45.4	5.7	4.9	58.2
25 Heat Stability Viscosity-average molecular weight (Mv $\times 10^{-3}$)	Before treatment	22	22	-	22	-	22	-
	After treatment	21	16	-	21	-	17	-
	Decrease	1	6	-	1	-	5	-

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As described above, the composition of this invention can be advantageously used as medical cases such as those used in artificial dialyzers, artificial lungs, and blood transfusion sets, which are to be undergo radiation sterilization (generally, gamma ray or electron beam sterilization).

35 Claims

1. A radiation resistant polycarbonate resin composition which comprises:
 - (A) an aromatic polycarbonate resin containing an aromatic polycarbonate polymer or oligomer having in its molecular chain a structural unit derived from a halogenated bisphenol, wherein said aromatic polycarbonate resin has a halogen content of from 0.1 to 5% by weight;
 - (B) a polyalkylene compound
 - (a) selected from poly(alkylene glycol)s, poly(alkylene glycol)esters, poly(alkylene glycol)ethers, and poly(alkylene glycol) silyl ethers, and
 - (b) represented by the following formula (1):

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wherein

R represents hydrogen, a methyl or an ethyl group, X¹ and X² each represents hydrogen, an alkyl group having 1 to 10 carbon atoms, an acyl group having 2 to 35 carbon atoms, or a -Si(R¹)₃ group, wherein the R's which may the same or different, each represents an alkyl group having 1 to 10 carbon atoms or an aryl group having 6 to 10 carbon atoms, and m is an integer up to 1000,

wherein (B) is present in an amount from 0.1 to 5% by weight, and

- (C) 0.01 to 3% by weight based on the weight of component (A) of at least one release agent selected from esters of saturated higher fatty acids with saturated alcohols, and low molecular weight polyolefins.

2. A polycarbonate resin composition as claimed in claim 1, wherein the amount of said release agent is from 0.1 to 1% by weight.
3. A polycarbonate resin composition as claimed in claim 1, which further comprises 0.001 to 0.1% by weight based on the weight of component (A) of at least one heat stabilizer selected from phosphorous acid and phosphorous esters.
4. A polycarbonate resin composition as claimed in claim 1, wherein said polyalkylene compound is a poly(alkylene glycol)ester.
- 10 5. A polycarbonate resin composition as claimed in claim 1, wherein said halogenated bisphenol is 2,2-bis(4-hydroxy-3,5-dibromophenyl)propane.

Patentansprüche

- 15 1. Bestrahlungsbeständige Polycarbonatharz-Zusammensetzung, umfassend:
 - (A) Ein aromatisches Polycarbonatharz, enthaltend ein aromatisches Polycarbonatpolymer oder -oligomer mit einer von einem halogenierten Bisphenol abgeleiteten Struktureinheit in der Molekülkette, wobei das aromatische Polycarbonatharz einen Halogengehalt von 0,1 bis 5 Gew.-% hat;
 - (B) eine Polyalkylenverbindung
 - (a) ausgewählt aus Poly(alkylenglykolen), Poly(alkylenglykol)estern, Poly(alkylenglykol)ethern und Poly(alkylenglykol)silylthern, und
 - (b) der allgemeinen Formel (1):

25 $X^1\text{-O-(CH}_2\text{-CHR-O)}_m\text{-X}^2 \quad (1)$

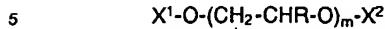
worin
R Wasserstoff, eine Methyl- oder eine Ethylgruppe bedeutet, X^1 und X^2 jeweils Wasserstoff, eine Alkylgruppe mit 1 bis 10 Kohlenstoffatomen, eine Acylgruppe mit 2 bis 35 Kohlenstoffatomen oder eine $\text{-Si}(R^1)_3$ -Gruppe bedeuten, wobei die R^1 -Reste, die gleich oder verschieden sein können, jeweils eine Alkylgruppe mit 1 bis 10 Kohlenstoffatomen oder eine Arylgruppe mit 6 bis 10 Kohlenstoffatomen bedeuten, und m ist eine ganze Zahl von bis zu 1000,
worin (B) in einer Menge von 0,1 bis 5 Gew.-% vorliegt, und

 - (C) 0,01 bis 3 Gew.-%, bezogen auf das Gewicht der Komponente (A) wenigstens eines Trennmittels, ausgewählt aus Estern von gestättigten höheren Fettsäuren mit gesättigten Alkoholen und niedrigmolekulargewichtigen Polyolefinen.
2. Polycarbonatharz-Zusammensetzung gemäß Anspruch 1, in welcher die Menge des Trennmittels 0,01 bis 1 Gew.-% beträgt.
3. Polycarbonatharz-Zusammensetzung gemäß Anspruch 1, die weiterhin 0,001 bis 0,1 Gew.-%, bezogen auf das Gewicht der Komponente (A) wenigstens eines Wärmestabilisators, ausgewählt aus Phosphorsäure und Phosphorsäureestern umfaßt.
4. Polycarbonatharz-Zusammensetzung gemäß Anspruch 1, in welcher die Polyalkylenverbindung ein Poly(alkylenglykol)ester ist.
5. Polycarbonatharz-Zusammensetzung gemäß Anspruch 1, in welcher das halogenierte Bisphenol 2,2-Bis(4-hydroxy-3,5-dibromophenyl)propan ist.

Revendications

1. Composition de résine de polycarbonate résistante au rayonnement, laquelle comprend:
 - (A) une résine de polycarbonate aromatique contenant un polymère ou oligomère de polycarbonate aromatique présentant dans sa chaîne moléculaire une maille provenant d'un bisphénol halogéné, ladite résine de polycarbonate aromatique ayant une teneur en halogène comprise entre 0,1 et 5 % en masse;
 - (B) un composé polyalkylène

(a) choisi parmi les polyalkylèneglycols, les esters de polyalkylèneglycols, les éthers de polyalkylèneglycols et les silyléthers de polyalkylèneglycols et
 (b) représenté par la formule (1) suivante :



dans laquelle

R représente l'atome d'hydrogène, un groupement méthyle ou éthyle, X¹ et X² représentent chacun l'atome d'hydrogène, un groupement alkyle ayant de 1 à 10 atomes de carbone, un groupement acyle ayant de 2 à 35 atomes de carbone ou un groupement -Si(R¹)₃, dans lequel les radicaux R¹ qui peuvent être identiques ou différents représentent chacun un groupement alkyle ayant de 1 à 10 atomes de carbone ou un groupement aryle ayant de 6 à 10 atomes de carbone, et m représente un nombre entier allant jusqu'à 1000,

10 (B) étant présent en une quantité comprise entre 0,1 et 5 % en masse ; et

15 (C) de 0,01 à 3 % en masse par rapport à la masse du composant (A) d'au moins un agent de démontage choisi parmi les esters d'acides gras supérieurs saturés avec des alcools saturés, ainsi que les polyoléfines de masse moléculaire faible.

2. Composition de résine de polycarbonate selon la revendication 1, dans laquelle la quantité dudit agent de démontage est comprise entre 0,1 et 1 % en masse.

20 3. Composition de résine de polycarbonate selon la revendication 1, laquelle comprend de plus de 0,001 à 0,1 % en masse par rapport à la masse du composant (A) d'au moins un stabilisant à la chaleur choisi parmi l'acide phosphoreux et les esters phosphoreux.

25 4. Composition de résine de polycarbonate selon la revendication 1, dans laquelle ledit composé polyalkylène est un ester de polyalkylèneglycol.

30 5. Composition de résine de polycarbonate selon la revendication 1, dans laquelle ledit bisphénol halogéné est le 2,2-bis(4-hydroxy-3,5-dibromophényl)propane.

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